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Oil spill in the Río de la Plata estuary, Argentina: 1. Biogeochemical assessment of waters, sediments, soils and biota

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The Oil spill impact in the Río de la Plata was evaluated by HRGC and multivariate techniques applièd to waters, sediments and biota.

Abstract

Aliphatic (ALI) and aromatic (ARO) hydrocarbon concentrations, composition and sources were evaluated in waters, sediments, soils and biota to assess the impact of ~1000 tons of oil spilled in Río de la Plata coastal waters. Total ALI levels ranged from 0.4–262 μg/l in waters, 0.01–87 μg/g in sediments, 5–39 μg/g in bivalves, 12–323 μg/g in macrophytes to 948–5187 μg/g in soils. ARO varied from non-detected 10 μg/l, 0.01–1.3 μg/g, 1.0–16 μg/g, 0.5–6.9 μg/g to 22–67 μg/g, respectively. Offshore (1, 5, 15 km) waters and sediments were little affected and contained low background hydrocarbon levels reflecting an effective wind-driven transport of the slick to the coast. Six months after the spill, coastal waters, sediments, soils and biota still presented very high levels exceeding baseline concentrations by 1–3 orders of magnitude. UCM/resolved aliphatic ratio showed a clear trend of increasing decay: coastal waters (3.3) < macrophytes (6.7) < soils (9.4) < offshore sediments (13) < coastal sediments (17) < clams (52). All environmental compartments consistently indicated that the most impacted area was the central sector close to Magdalena city, specially low-energy stream embouchures and bays which acted as efficient oil traps. The evaluation of hydrocarbon composition by principal component analysis indicated the predominance of biogenic (algae, vascular plant cuticular waxes), background anthropic, pyrogenic and diagenetic hydrocarbons, offshore and in non-impacted coastal sites. In contrast, polluted stations presented petrogenic signatures characterized by the abundance of isoprenoids, low molecular weight *n*-alkanes and methylated aromatics in different stages of alteration. The petrogenic/biogenic ratio (< *n*-C22 + isoprenoids/*n*-C15 + *n*-C17 + > *n*-C23) and petrogenic/pyrogenic relationship (methylated/unsubstitued PAH) discriminated the samples according to the different degree of impact. The following paper present the results of the study of the progress of hydrocarbon disappearance in sediments and soils 13 and 42 months after the spill.

Keywords: Oil spill; Hydrocarbon; Biogeochemistry; Río de la Plata

1. Introduction

Petroleum hydrocarbons are ubiquitous contaminants in the aquatic environment, specially in major rivers and estuaries which support a strong urban-industrial development. Chronic spillages from land-based facilities, ports and vessels, crude effluent discharges and accidental spills, continuously introduce large amounts of hydrocarbons to these ecosystems. According to local environmental characteristics and the distinct physico-chemical properties of the

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numerous petroleum components, hydrocarbons undergo a differential fractionation in the environment. After the initial steps of slick spreading, evaporation, dissolution of smaller molecules, emulsification, photochemical oxidation of susceptible aromatics and biodegradation of labile components, a large percentage (>30–50%) of spilled hydrocarbons enriched in heavier more recalcitrant compounds are deposited in bottom sediments, beaches and soils which then act as long-term reservoirs and secondary sources (Albaigés, 1980; Gearing et al., 1980; Lee, 1980; Olsen et al., 1982).

The Río de la Plata estuary is a funnel-shaped, turbid, coastal-plain estuary 300 km long, 30–220 km wide and 0.5–25 m deep with a total surface area of 35,000 km^2 (Fig. 1). In spite of the large dimensions and dilution capacity of the estuary, the vast urban-industrial zone developed in the first 100 km of the Argentinean coast produced a significant impact on the coastal area (review in Colombo 2000). Polluted waters and toxic materials are discharged daily to the estuary via untreated effluents close to Buenos Aires city. The hydrocarbon composition of bottom sediments (Colombo et al., 1989) show the dominance of petrogenic sources in tributaries and nearby coastal areas affected by petrochemical effluents, tanker ballast washings and furtive spillages. Offshore sediments denote the contribution of vascular-plant waxes and pyrogenic polycyclic aromatic hydrocarbons (PAHs) transported from major fossil fuel combustion sources. The hydrocarbon load to the estuary is also evident in biota such as a specialized detritivorous fish which present clear petrogenic aliphatic signatures in the muscle (Colombo et al., 2000).

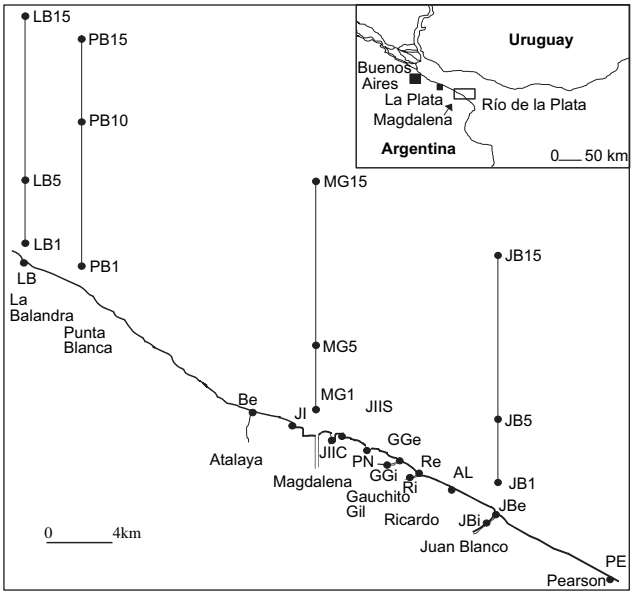

Fig. 1. Study area and station location along offshore transects and the shoreline of the Río de la Plata estuary. Station abbreviations are given in Table 1.

In addition to these chronic hydrocarbon inputs, on January 15th 1999, the collision of the cargo ship Sea Parana and the tanker Estrella Pampeana in the Intermediate Channel, 20 km away from the Argentinean coast, produced a spill of ~1000 tons of oil. In the next 2 days, strong southeast winds pushed the uncontrolled slick against the shoreline of Magdalena, located 120 km SE from Buenos Aires in the less impacted intermediate freshwater sector of the estuary (Fig. 1). This is a temperate (mean 18 °C), dynamic coastal environment modeled by the strong freshwater discharge, small tides and winds. The coast physiognomy is dominated by sandy beaches colonized by water grasses and macrophytes, particularly developed in low areas like stream embouchures and bays, and young soils covered by grass and a patchy forest of small autochthonous species. The massive oiling of the beach, soils and even trees was favored by the flood driven by intense SE winds. The cleaning activities were limited to a partial mechanical removal of major oil patches on the beach and most affected vegetation.

In order to evaluate the impact produced, a monitoring project was coordinated by the Buenos Aires Environmental Policy Agency (SPA) and the Natural Sciences Faculty from the National University of La Plata. This paper presents the results of the biogeochemical assessment of hydrocarbons in waters, sediments, soils and biota. Specific objectives were: (a) to quantify hydrocarbon levels in the different environmental compartments; (b) to compare results with previous baseline levels; (c) to identify critical areas; (d) to characterize hydrocarbon composition and sources. The following paper presents the results of the study of the progress of hydrocarbon attenuation in sediments and soils 13 and 42 months after the spill. Both papers are intended to illustrate the fate of oil residues and the natural recuperation capacity of this southern temperate estuary.

2. Methods

Sampling was performed 6 months after the spill in July 1999 in offshore waters over four 15-km transects, and along the coast covering the most impacted area (Fig. 1). A total of 26 stations were visited, 12 offshore and 14 over 45 km of shoreline (Table 1), for the collection of surface waters (1–4 l in amber glass bottles), sediments and soils (Hydro-Bios stainless steel grab sampler and spatula in 300 ml glass jars), macrophytes (*Schenoplectum californicus*) and Asiatic clams (*Corbicula fluminea*). All glass material was pre-cleaned for trace organic analysis (detergent, distilled water, 10% nitric acid, acetone). Samples were maintained in portable